Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 117 (2014) 191–197

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Spectroscopic properties of Sm^{3+} doped lead bismosilicate glasses using Judd–Ofelt theory

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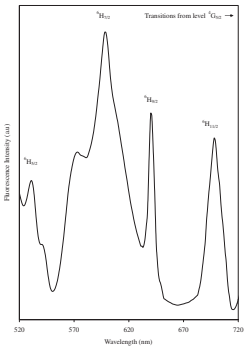
HIGHLIGHTS

- Optical properties of Sm^{3+} doped lead bismuth silicate glasses have been studied.
- Transition $^4G_{5/2} \rightarrow {}^6H_{7/2}$ is responsible for reddish-orange luminescence.
- Covalency decreases with decrease in bismuth content.

GRAPHICAL ABSTRACT

Emission spectrum of $20PbO{\cdot}69.5Bi_2O_3{\cdot}10SiO_2{\cdot}0.5Sm_2O_3$ (PBSS1) sample.



ARTICLE INFO

Article history:
Received 1 January 2013
Received in revised form 29 July 2013
Accepted 2 August 2013
Available online 11 August 2013

Keywords:
Glasses
Spectroscopy
Judd–Ofelt theory
Sm^{3+} doped glasses
Optical properties

ABSTRACT

The spectroscopic properties of Sm^{3+} ions in lead bismosilicate glasses (PBSS) as a function of bismuth oxide were investigated using optical absorption and fluorescence spectra. These glasses have shown strong absorption and emission bands in the near infrared and visible region respectively. From the measured absorption spectra, Judd–Ofelt intensity parameters Ω_2, Ω_4 and Ω_6 were determined by applying least square analysis method. The variation of Ω_2 and Ω_6 with Bi_2O_3 content has been attributed to changes in the asymmetry of the ligand field at the rare earth ion site and to the changes in the rare earth oxygen (RE-O) covalency. The variation of Ω_4 with Bi_2O_3 content has been attributed to rigidity of the samples. Using the Judd Ofelt intensity parameters the other radiative properties like radiative transition probability, radiative life time, branching ratio and the stimulated emission cross-sections of prepared PBSS glasses have been calculated. The values of radiative properties indicate that Sm^{3+} ions emit intense reddish-orange emission ($^4G_{5/2} \rightarrow {}^6H_{7/2}$) under excitation at 450 nm wavelength.

Introduction

Glasses doped with various rare earth ions are important materials for optical detector, optical fiber amplifiers, wave guide laser and fluorescent display devices [1–3]. Recently, research focus on rare-earth doped glasses is not only limited to infrared optical devices, but also there is a growing interest in visible optical devices [4,5]. With the increasing demand of various fluorescent devices and visible laser, further investigations in rare-earth ions such as Sm^{3+} ions, are becoming more significant [6,7]. In general, the optical and spectroscopic properties of rare earth ions are strongly dependent on host materials. The host glass materials should have high refractive index with good chemical and thermal stability along with low melting temperature of heavy metals in order to become more practically useful in industries. Many potential host

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http://dx.doi.org/10.1016/j.saa.2013.08.006

materials for rare earth ions have been developed. One of the preferred host materials is oxide glasses which are chemically durable, thermally stable, optically transparent at the excitation and lasing wavelengths [8]. Glasses based on heavy metal oxides (such as Bi_2O_3) have received increased attention due to their manifold possible applications in the field of glass ceramics, layers for optical, optoelectronics devices, thermal and mechanical sensors, reflecting windows, etc. [9,10]. The large polarizability of bismuth makes it suitable for possible non linear optical devices and environmental guide lines [11]. Also due to maximum phonon energy of bismuth, the non radiative losses to the lattice will be small and the fluorescence quantum efficiency will be high [12,13]. Wide transmitting window in the optical region having sharp cut-off in both UV–VIS and IR region make these glasses useful in spectral devices. Further, the increase of Bi_2O_3 into the glass improves the glass stability against crystallization. Presently, heavy metal lead (Pb) has also been chosen as it has large glass forming region, high refractive index, good physical and chemical stability and large window transmission. Such glasses could represent one of the potential host materials for several rare earth dopants with improved quantum efficiency of luminous bands and hence suitable for various laser applications. Further, Judd–Ofelt theory [14,15] has been employed to calculate the intensities of f–f transition in the absorption spectra of the rare earth ion. According to this theory, the strength of an f–f transition is proportional to the sum of the products of three intensities parameters Ω_λ ($\lambda = 2,4,6$) (which are dependent on the environment of the impurity rare-earth ion) and the squares of the matrix elements U_t of the transition under consideration that are weakly affected by the environment. Experimental investigations of absorption spectra of rare earth ions in different matrices [16] have revealed that the oscillator strengths for the specific transitions of rare earth ions depend more strongly on the structural features of materials and on the chemical nature of the ligands surrounding the rare earth ions. Once the experimental values of the oscillator strengths are determined from the integrated absorption coefficient, the intensity parameters can be obtained. When the phenomenological parameters Ω_λ are calculated, it is possible to derive the strength of any absorption or emission transition, as well as the stimulated emission cross-section, the fluorescence branching ratio from level J to J′, and the radiative life time of an excited level. Such spectral studies give valuable information about the structure and bonding in glass and radiative and non radiative properties of rare earth ions doped in glass matrix. This information is essentially required while developing new optical devices.

Therefore, the purpose of the present study is to introduce the upgraded lasing material by including the heavy metals PbO and Bi_2O_3 in silicate glasses. Various intensity parameters and spectroscopic properties viz, emission cross-section, radiative life time, and branching ratio of Sm^{3+} ions doped lead bismosilicate glasses are determined from the absorption and emission spectra using Judd–Ofelt theory. The glasses with two glass formers yield higher quantum efficiency therefore efforts have been made to optimize the best ion-host configuration for improved laser efficiency.

Experimental

Glasses having compositions $20PbO{\cdot}(79.5 - x)Bi_2O_3{\cdot}xSiO_2$ ($10 \leqslant x \leqslant 50$, mol%) doped with 0.5 mol% of Sm^{3+} ions were prepared by melt quench technique. Appropriate amount of AR grade chemicals (PbO, Bi_2O_3, SiO_2 and Sm_2O_3) having purity above 99.99% were weighed on 0.001% accuracy and mixed thoroughly. The raw mixed materials were melted in a muffle furnace in air (at 1150 °C for 40 min). The crucible was shaken frequently after every 10 min for the homogeneous mixing of all the constituents. The melt was quenched at room temperature by pouring between two stainless steel plates. The quenched samples were annealed to minimize the internal strain and then allowed to cool slowly to room temperature. Due to lead content in the composition of host glass, it appeared transparent yellow color. The exact composition along with the codes of the samples is given in Table 1. The samples were finally polished for spectral and other investigations. The amorphous nature of the glasses was confirmed by recording the X-ray diffraction pattern using Mini Flex Desktop X-ray Difractometer with Cu Kα line of wavelength at the scanning rate of 2°/min and 2θ was varied from 10° to 80°. The refractive index (n) of the prepared samples was measured by the Brewster angle method using He–Ne laser (633 nm). The density (D_g) of all the glasses was measured by using Archimedes principle with xylene as immersing liquid. The relation used is

$$D_g(\mathrm{g/cm^3}) = \frac{W_a}{W_a - W_b} D_x \quad (1)$$

where W_a is the weight of glass sample in air, W_b is the weight of glass sample when immersed in xylene and D_x is the density of xylene (0.86 gm/cm^3). The optical absorption spectra of all the polished samples were recorded on a Varian-Carry 5000 spectrophotometer in the range 300–3200 nm. The emission spectra were recorded using Fluoro-max-3 Fluorimeter with Xe arc lamp as the excitation source at wavelength of 450 nm.

Results and discussion

Density and molar volume

Various physical properties of all glasses as a function of Bi_2O_3 content were determined from the experimental data and are listed in Table 1. It is clearly observed that density decreases monotonously when Bi_2O_3 is replaced by SiO_2 in the glass. This may be due to greater molar mass of Bi_2O_3 (438.96 g) than that of SiO_2 (60.08 g). The decrease in molar volume on the other hand shows that addition of SiO_2 may contract the structure of the loose network in the studied glass. Also the smaller values of radii and bond length of SiO_2 than that of Bi_2O_3 results in decrease in the volume of these glasses. In general, it is expected that the density and molar volume should show opposite behavior to each other. According to Pan et al. [17], the Bi–O bond is more ionic in nature which may result in the decrease in molar volume of the present glasses.

Optical basicity

During recent years the optical basicity has been successfully used to correlate a range of properties of glass with chemical composition. The optical basicity of a material can be experimentally determined using UV probe ion spectroscopy. It was found that the frequency of the UV absorption band shifts gradually with composition. This effect known as the "nephelauxetic" effect is connected with orbital expansion of the probe ion brought about by electron donation of the oxygens of the glass. The optical basicity (Λ) addresses the ability of oxide glass in contributing the negative charges in the glass matrix. In other words it defines the electron donating power of the oxygen in the oxide glass. It is well known that free oxygen has the ability to donate negative charge of 2, but when participating in the chemical bond with the surrounding cations in the matrix, its charge rendering power to the metal ions becomes less. The theoretical optical basicity can be calculated by the relation proposed by Duffy and Ingram [18].

$\Lambda_{th} = X_1\Lambda_1 + X_2\Lambda_2 + X_3\Lambda_3 + ,\ldots\ldots..,+ X_n\Lambda_n$, where $X_1, X_2, \ldots\ldots.., X_n$ are equivalent fraction based on the amount of oxygen each oxide